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**DIELECTRIC CONSTANT MEASUREMENTS
ON LEAD AZIDE SINGLE CRYSTALS**

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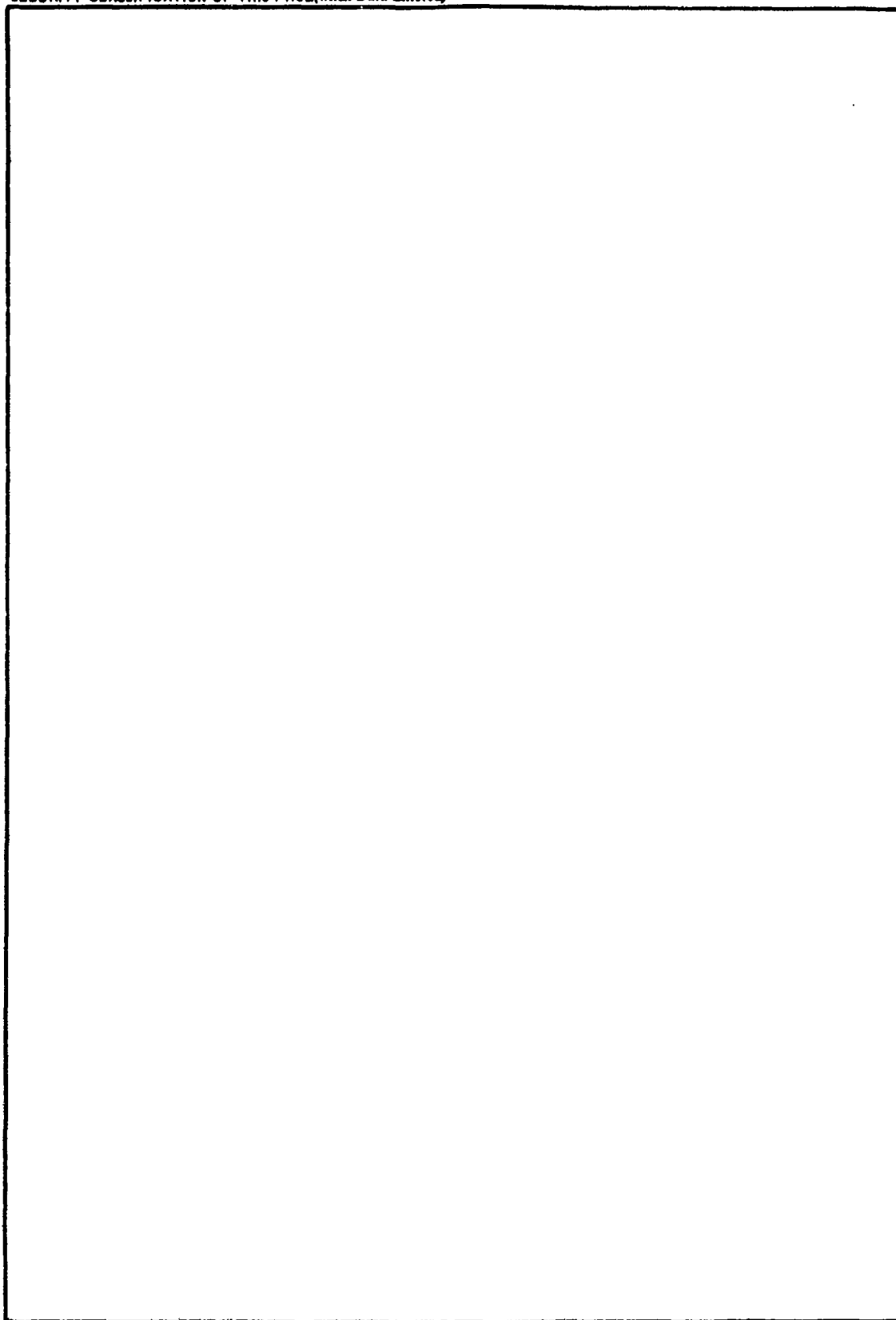
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INTRODUCTION

Lead azide is a widely used primary explosive whose intrinsic solid state properties are being investigated in order to help explain its sensitivity. Experimental data from both optical and electrical measurements established the need for a knowledge of the dielectric properties of this material. For example, optical absorption studies on crystals and thin films show an abrupt increase in absorption at 390 nm, with a strong absorption peak in the edge at 375 nm and additional structure at higher energies (ref 1). These peaks are attributed to one of four types of excitons, with final interpretation clearly dependent on the dielectric constant. A value for the dielectric constant is also needed to calculate internal electric fields resulting from applied external fields for such studies as electrostatic initiation (ref 2) and photoelectronic initiation (ref 3).

Although existing dielectric data have been obtained only on pressed powder samples of varying densities (ref 4), the results when extrapolated to crystal density, do suggest that lead azide has a large dielectric constant as compared to most ionic materials.

The possibility of large dielectric anisotropies also exists if extrapolations are made from other fundamental constants such as compressibilities (ref 5), thermal expansion coefficients (ref 6), and indices of refraction (ref 7).

Thus, it was felt that a study of the dielectric properties would aid in interpreting existing data and perhaps give additional insight into the electrical properties of lead azide.

EXPERIMENTAL

Single crystals of lead azide were grown from a 20% aqueous ammonium acetate solution by slow cooling (ref 8). An analysis of inorganic impurities, made on the residue of several thermally decomposed crystals, showed the major impurities to be Si (30 ppm), Al (6.5 ppm), and B (2.6 ppm). The crystal structure of samples grown by this technique has recently been refined by Choi et al. (ref 9).

For dielectric measurements a sample was first oriented along a specific crystallographic direction by the back-reflection Laue technique and cut into plates using a string saw wetted with a weak solution of ceric ammonium nitrate. The plates were mechanically polished with 1 micron aluminum oxide polishing compound to obtain nearly flat, parallel surfaces. Plate areas ranged from 0.1 to 0.2 cm² and the thickness varied from 0.4 to 0.7 mm with a maximum variation in thickness across the sample of 5%.

Evaporated gold electrodes backed with either platinum foil or silver paint were used to make electrical contact to the sample. Silver paint applied directly to the lead azide crystals also gave consistent results. Electrode areas were measured using a photo-microscope to obtain an enlarged picture of the electrode superimposed on a grid of known dimensions.

Capacitance and dissipation values were recorded, using both a GR1615-A and GR716-C type capacitance bridge in order to cover the frequency range from 10^2 to 10^6 Hz. An amplifier and oscilloscope served for null detection. The electrode assembly consisted of parallel brass electrodes $3/4$ inches in diameter with one movable electrode connected to a micrometer. Both electrodes were surrounded by an insulated metal can which provided both electrical and thermal shielding. Cooling and heating over the range from -100°C to $+100^\circ\text{C}$ was accomplished by flowing temperature controlled dry nitrogen through the fixture. In a separate experiment, with the sample mounted in a dewar between two fixed electrodes, a temperature of 100 K was attained. With the dewar arrangement, a low noise PAR amplifier and a General Radio synchronous detector were used for null detection. Temperatures were monitored in both systems with a platinum resistor.

Since the crystal area, A_s , was in all cases smaller than the brass electrode area, A_e , the capacitance, C_1 , with the sample between the electrodes is given by

$$C_1 = \frac{A_s (k'-1)}{d_s} + \frac{A_e}{d_s} + C_x \quad (1)$$

where d_s is the sample thickness and C_x the stray capacitance. With the sample removed, the capacitance, C_0 , is given by

$$C_0 = \frac{A_e}{d_s} + C_x \quad (2)$$

Subtracting equation 2 from equation 1 gives an expression for the dielectric constant k' :

$$k' = (C_1 - C_0) \frac{d_s}{A_s} + 1 \quad (3)$$

Dielectric loss, k'' , is calculated from the measured dissipation factor, D , using the relationship $k'' = Dk'$. A maximum inaccuracy of 10% in the value of the dielectric constant is due to errors in measuring the small surface area of the evaporated electrodes, the lack of parallel surfaces, and unaccounted-for edge capacitances.

For comparison purposes the dielectric constants of several other azides in single crystal form were measured and are also reported.

RESULTS

The dielectric constants of lead azide ($\text{Pb}(\text{N}_3)_2$) along the three unit cell axes are given in table 1 to within the experimental uncertainty of 10%. These values are frequency independent at room temperature over the range 10^2 to 10^6 Hz. The dissipation factor is small for each orientation ($D < 10^{-3}$), indicating negligible loss over this frequency range. At a fixed frequency of 10^3 Hz, the variation of the dielectric constant with temperature, dk'/dt , has a positive slope that changes by less than 4% over the temperature range from 100 K to 370 K.

As a check on the apparatus, several reference crystals were cut and polished to the approximate size of the lead azide crystals. The materials measured were TlCl ($k' = 32$), KCl (5.03), calcite (8.0), and ADP (56). The measured values agreed, within the accuracy of the system, with the accepted values (ref 10). Several other azides which were available in singlecrystal form were also measured to make comparisons to the lead azide case. A summary of the dielectric constants and losses for TlN_3 , NaN_3 , and KN_3 is also shown in table 1. A brief description of the preparation of each of these samples is included here: (1) The platelet of TlN_3 , grown from water by slow cooling, was of poor optical quality, having a striated surface. X-ray Laue photographs gave a single crystal pattern but the reflections were streaked. Silver paint was used as an electrode. Due to the poor quality of the crystal, only a single measurement was made at 1 KC. (2) The sodium azide platelet, grown from water by slow evaporation, had a $[111]$ rhombohedral surface plane. Evaporated gold electrodes were used for both NaN_3 and KN_3 because the silver paint was found to react, causing the capacitance and loss to change with time (ref 3). The KN_3 crystals were grown from the melt (ref 11) and then prepared into platelets in the same manner as lead azide. The KN_3 results agree well with those previously published by Laska of 6.6 (ref 12) and Danemar of 7.3 ± 1.0 (ref 13).

Table 1. Dielectric constants and losses versus orientation for those azide crystals examined.

<u>Material</u>	<u>Orientation</u>	<u>k'</u>	<u>k''</u>	<u>ω</u>
Pb(N ₃) ₂	<100>	17 ±1.7	<2x10 ⁻²	10 ² -10 ⁶
	<010>	120 ±12.0	<2x10 ⁻¹	10 ² -10 ⁶
	<001>	40 ±4.0	<4x10 ⁻²	10 ² -10 ⁶
TlN ₃	<100>	50 ±10	2.5	10 ³
NaN ₃	<111>	17 ±2.0	<10 ⁻²	10 ³ -10 ⁶
KN ₃	<100>	8.7 ±0.5	<10 ⁻²	10 ⁵ -10 ⁶
	<001>	5.6 ±0.5	<10 ⁻²	10 ⁵ -10 ⁶

DISCUSSION

The lack of any dielectric relaxation up to one megahertz and the insensitivity of the dielectric constant to temperature seems to rule out the possibility that the large dielectric constants in lead azide could be the result of space charge or interfacial polarizations. A linear extrapolation of pressed powder densities to single crystal density gives a dielectric constant of 17, which is also in general agreement with the crystal results. Pressed powders also show no dispersion over the frequency range of 10³ to 10⁶ Hz. High frequency dielectric constants calculated from the indices of refraction along the a, b, and c crystallographic axes are, respectively, 3.5, 7.0, and 5.0, having the same directional dependence as the low frequency values.

The large difference, however, between the high and low frequency dielectric constant of lead azide indicates that the major contribution to the total polarization is a result of atomic displacements. Semi-quantitative calculations were performed to determine which of the possible polarizations within the lattice could result in the observed anisotropies. The results of these calculations and their relationship to the crystal structure of lead azide are discussed below.

The atomic arrangement of atoms within the orthorhombic unit cell (a = 11.31Å, b = 16.25Å, c = 6.63Å), projected in the a-b plane, is shown in figure 1. There are 12 molecules per unit cell with two different lead sites and four different azide sites. Additional

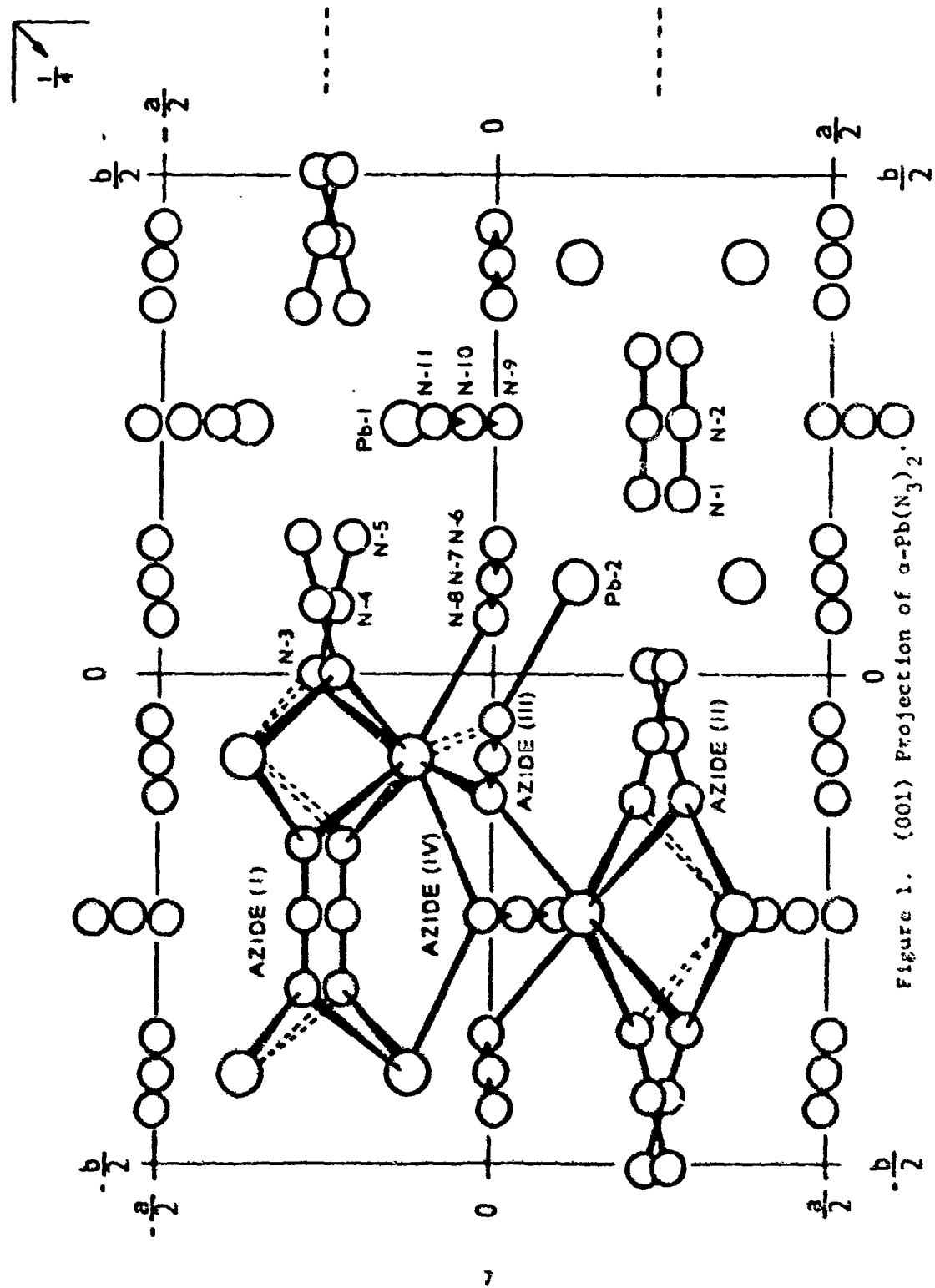
details concerning the structure are available elsewhere (ref 14). In this lattice, polarizations of the azide molecules must be considered in addition to movements of the sublattices relative to each other. Calculations show that polarizations due to bending or rotations of the azide ion have the wrong directional dependence and that polarizations due to sublattice movements have a nearly isotropic directional dependence. Only in the special case where the force constants bonding the lead atoms to azide IV are reduced to 1/10th of the force constants assumed for the remaining azide bonds can the proper directional anisotropy be obtained; however, this assumption seems physically unrealistic.

The polarizations which fit the observed anisotropy result from distortions of the intra-azide bond lengths producing a net dipole moment of the molecule. Assuming similar force constants between all azide ions and nearest neighbor lead atoms, the ratio of calculated polarizabilities agrees well with the observed anisotropy in the dielectric constants.

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